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An electroanalytical study of the composition of molten sodium metaphosphate

E. FRANKS,* D. INMAN

Nuffield Research Group in Extraction Metallurgy, Department of Metallurgy, Imperial College, London, S.W.7.

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Phosphate glasses are known to be mixtures of chain phosphates. The presence of the lower polymers has been confirmed by electrochemical techniques and the proportions of the orthophosphate monomer in sodium metaphosphate melts have been estimated at temperatures between 660–810°C. The orthophosphate had not been detected in phosphate glasses using paper chromatography, but it is considered that quenching tends to increase polymerization and thus causes loss of the monomer.

Introduction

Glass-forming alkali metal phosphate melts can be considered as mixtures of straight-chain phosphorus-oxygen polymeric anions (having the general formula $(P_nO_{3n+1})^{(n+2)-}$) in dynamic equilibrium and the equivalent number of alkali metal cations. The compositions of a number of glass-forming sodium phosphate melts have been determined by Westman and co-workers [1, 2] as well as by Meadowcroft and Richardson [3]. In these investigations, the melts were quenched and the frozen-in constituent polymers separated and determined by means of paper chromatography following aqueous extraction. The determined composition differed from the predicted Flory polymer distribution based on a series of equilibria of the type

$$2(P_nO_{3n+1})^{-n-2} = (P_{n+1}O_{3n+4})^{-n-3} + (P_{n-1}O_{3n-2})^{-n-1} \qquad (1)$$

(e.g. the amounts of the lower polymers were less than those expected on the basis of the ideal Flory distribution). Indeed, negligible amounts of the monomer (PO_4^{3-}) were found in the glasses formed from melts having $Na_2O : P_2O_5$ ratios up to 5 : 3 (average chain length $\bar{n}$ of 3).

The development of *in situ* methods for determining the compositions of these polymeric materials *in the molten state* is obviously desirable, as changes are always liable to occur during quenching, if the exchange rates of the equilibria mentioned above are high enough. In the present work, the behaviour of the sodium metaphosphate glass-forming melt ($\bar{n} > 50$) was examined, over the temperature range 660–810°C using *in situ* electrochemical techniques. As will become evident in the latter part of this paper, these techniques are particularly suitable for determining melt constituents present at low concentrations. It was found that phosphorus was formed as the product of the direct (primary) electroreduction of a reducible species present (at low concentration) in the glass forming melt. The possibility that the latter was the lowest polymer of the series present in the melt was investigated by comparing the electrochemical behaviour of solutions of low polymer phosphates in molten halide solvents, with that of the undiluted phosphate melt.

Experimental

In the initial experiments pure anhydrous sodium trimetaphosphate, supplied by Albright and Wilson of Oldbury, was electrolysed in an atmosphere of dry argon. A dense graphite

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* Present address: Department of Science, Hendon College of Technology, London N.W.4.

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crucible acted both as a container and a non-polarizable anode, whilst the working electrode consisted of a 1 mm diameter tungsten rod enclosed in Supremax glass. The end of the electrode was ground flat and polished on a diamond pad. More details of the apparatus are given in [9].

The electrolysis current was obtained from a 350 V Farnell stabilized voltage supply through a Cambridge variable resistance box of 10,000 ohm maximum. The voltage between the tungsten electrode and the anode was displayed on a Tektronix Storage Oscilloscope 564.

Results and Discussion

Voltammetry of molten phosphates

Currents were increased and the steady state potentials attained by the cathode at each current were determined over the temperature range 660–810°C. The resultant polarograms are shown in Fig. 1. The first decomposition potential of −0·7V corresponds to the production of phosphorus, whilst the second decomposition potential of −2·1V was considered to correspond to the reduction of the sodium ion. In the diffusion current region, shown dotted, cyclic variations of voltage occurred and a mean value was taken as the steady state potential.

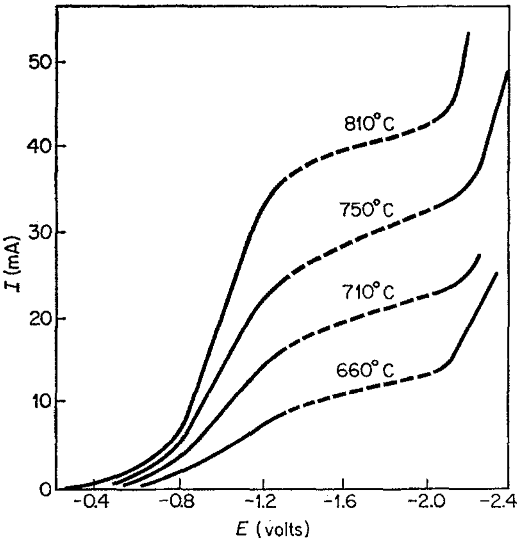

Fig. 1. E-I curves for molten $NaPO_3$ (E, potential of tungsten cathode vs. graphite pot).

Possible electrode processes were further investigated by means of decay curves, i.e. by switching off the current and eliminating the overvoltage due to the internal cell resistance. The results shown in Fig. 2 would seem to indicate that in addition to the process at −0·7V a further reduction occurs at about −1·5V.

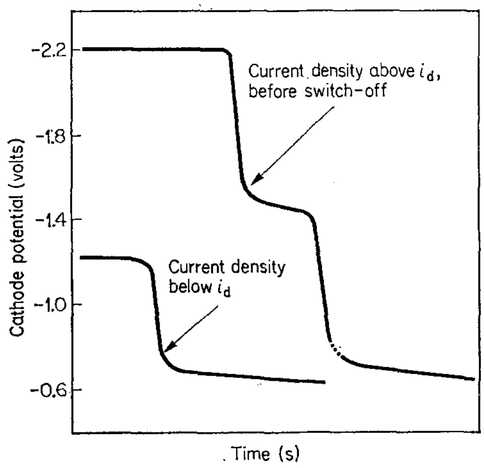

Fig. 2. Decay curves for molten $NaPO_3$ at 730°C.

Since the polarograms were not readily amenable to analysis chronopotentiometric methods were tried.

Chronopotentiometry of molten phosphates

Chronopotentiometry uses the change of electrode potential with time at constant applied current density as a basis for measurement. Sand [4] showed that the transition time τ (secs) is given by the relationship

$$\tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} n \mathrm{F} D^{\frac{1}{2}} C}{2i} \qquad (2)$$

for the linear diffusion of the electroactive species up to the electrode

where

C = concentration of reducible species (mole cm^{-3})

D = diffusion coefficient ($cm^2 sec^{-1}$)

F = the Faraday

n = number of electrons involved in unit reaction

i = constant applied current density (Acm^{-2}).

At current densities which caused the electrode potential to rise to about −1.0V, a first transition occurred. At higher current densities when the cathode potential was allowed to reach −2·0V, a second transition appeared. A typical chronopotentiogram is shown in Fig. 3.

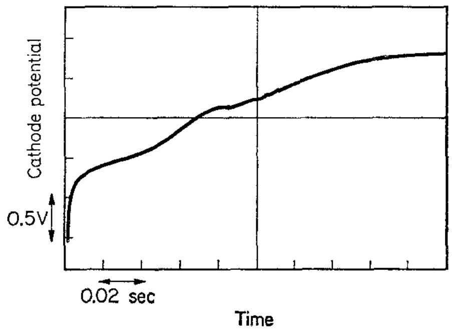

Fig. 3. Chronopotentiogram for molten $NaPO_3$.

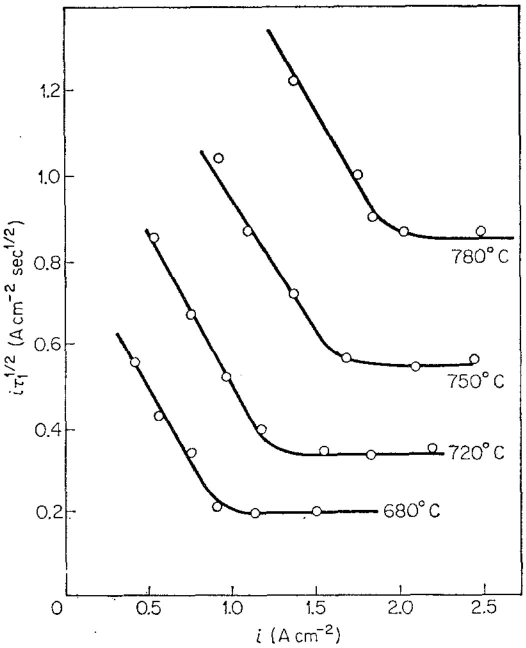

Fig. 4. Plots of $i\tau_1^{\frac{1}{2}}$ vs. i.

The transitions were examined over the temperature range 660°C to 810°C. At each temperature it was found that $i\tau^{\frac{1}{2}}$ decreased with increase in current density and finally tended to a constant value. Results are shown in Fig. 4 for the first transition. This type of behaviour was considered by Delahay and Berzins [5] to be a diagnostic criterion for the occurrence of a chemical reaction prior to the electroreduction; i.e. the electroactive species O is formed from Y:

$$\text{(a) } Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} O$$

followed by (b) $O + ne \longrightarrow R$

At low current densities the Y form will have time to change to the O form, whereas at high current densities the conversion is negligible during the pulse time. The constant $i\tau^{\frac{1}{2}}$ value is, therefore, a measure of the initial equilibrium value of O.

If the diffusion coefficients for the O and Y forms are assumed to be equal, then for $(k_f + k_b)^{\frac{1}{2}}\tau^{\frac{1}{2}} > 2$ the transition time is given by the equation

$$i\tau^{\frac{1}{2}} = \tfrac{1}{2}\pi^{\frac{1}{2}}\, nFC\, D^{\frac{1}{2}} - \tfrac{1}{2}\pi^{\frac{1}{2}}\, i/K(k_f + k_b)^{\frac{1}{2}} \qquad (3)$$

where K = equilibrium constant for reaction (a) i.e. k_f/k_b

In order to identify the reducible species and to define their concentrations, the lower polymer phosphates were examined as solutions in molten NaCl–KCl.

Chronopotentiometry of phosphate solutions

Using known concentrations of ortho, pyro, tripoly and metaphosphates in equimolar NaCl–KCl melt, it was found that cathodic transitions occurred at about the following potentials with reference to graphite:

PO_4^{3-}	−0·7V
$P_2O_7^{4-}$	−0·7V, −1·1V
$P_3O_{10}^{5-}$	−0·3V, −1·1V, −1·5V
PO_3^{-}	−0·7V −1·1V, −1·5V

These corresponding steps can be clearly seen in the decay curve for the tripolyphosphate in Fig. 5.

At any fixed concentration the $i\tau^{\frac{1}{2}}$ values obtained were constant; they did not show variations due to prior reactions in this case. For the higher polymers, the $i\tau^{\frac{1}{2}}$ corresponding to the first transition increased at the expense of the higher transitions as the temperature increased (indeed for the pyrophosphate additon the second transition had vanished at 750°C). These

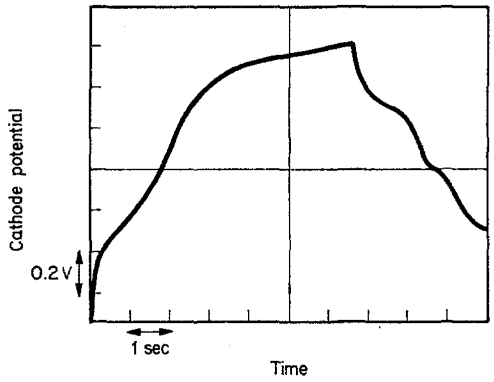

Fig. 5. Chronopotentiogram for $Na_5P_3O_{10}$ in NaCl-KCl.

results would seem to indicate that the reduction of the ortho, pyro and tripolyphosphate ions with reference to graphite occur at potentials of −0·7, 1·1 and 1·5V respectively; also, that the amount of orthophosphate monomer increases with temperature.

For the orthophosphate it was found that the reduction was a two-electron process; this agreed with the results of Lucas [6] for the first transition of the trimetaphosphate in LiCl–KCl eutectic. The diffusion coefficient for the orthophosphate ion in NaCl–KCl at 780°C was determined and a value of $8{\cdot}2 \times 10^{-6}$ cm^2 sec^{-1} obtained.

General Discussion

Orthophosphate concentrations in sodium metaphosphate melts

The above reductions of phosphate ions in halide melts can be compared with the electrolysis of the metaphosphate. In both cases the first transition occurs at −0·7V and the ion reducing at −1·5V is also present in the metaphosphate, as can be seen in Figs. 2 and 3.

On the basis of the these results, it would appear that the lower polymeric oxy-anions in the metaphosphate melt are reduced at increasing cathodic potentials as the chain length increases. The electrolysis mechanism is complex at the more cathodic potentials, but at −0·7V with regard to graphite, only the electroreduction of the orthophosphate ion occurs.

In equation 2 the value of the diffusion coefficient must be known in order to determine the concentration C. The former quantity was estimated in the following way. As part of the present investigation, a value of 6×10^{-6}cm^2 sec^{-1} was obtained for the diffusion coefficient of the Cu^{2+} ion in molten sodium metaphosphate at 750°C using chronopotentiometry. Sundheim [7] quotes values of $2\text{–}4 \times 10^{-5}$ cm^2 sec^{-1} for the Pb^{2+} ion in NaCl–KCl over the temperature range 700–800°C. Thus the Cu^{2+} ion might be expected to have a diffusion coefficient value of about 5×10^{-5} cm^2 sec^{-1} at 750°C in NaCl–KCl. Therefore, on this basis and the diffusion coefficient value of the orthophosphate ion of 8×10^{-6} cm^2 sec^{-1} at 780°C in NaCl–KCl, a value of 1×10^{-6} cm^2 sec^{-1} was estimated for the diffusion coefficient of this ion in the metaphosphate melt at 780°C. The variation of the diffusion coefficient with temperature was calculated from the Stokes–Einstein equation, i.e. by assuming that D is proportional to T/η (η = viscosity at temperature T.) Results are shown in Table 1. These results indicate that significant quantities of orthophosphate ions are present in molten metaphosphates.

Table 1. *Concentrations of* PO_4^{3-} *in metaphosphate melts*

Temp. (°*C*)	D (*cm*^{2} *sec*$^{-1}$)	$i\tau^{\frac{1}{2}}$(*Acm*$^{-2}$ *sec*$^{\frac{1}{2}}$)*	C (*mole cm*$^{-3}$)
680	$0{\cdot}34 \times 10^{-6}$	0·20	$1{\cdot}93 \times 10^{-3}$
720	$0{\cdot}54 \times 10^{-6}$	0·35	$2{\cdot}61 \times 10^{-3}$
750	$0{\cdot}77 \times 10^{-6}$	0·55	$3{\cdot}53 \times 10^{-3}$
780	$1{\cdot}0 \times 10^{-6}$	0·85	$4{\cdot}95 \times 10^{-3}$

* Values taken from Fig. 4

Chronopotentiometric experiments had suggested that depolymerization could occur prior to electroreduction and that the amount of the monomer increases with increase in temperature. Therefore it is possible for the orthophosphate ion to be lost by a polymerization process as the temperature drops.

Depolymerization in phosphate melts

The formation of the monomer can be considered as occurring via a series of steps of the form normally associated with chain polymer degradation

$$\text{i.e. } m_n \underset{k_p}{\overset{k_d}{\rightleftharpoons}} m_{n-1}+m_1$$

The overall reaction would be

$$\sum m_n \underset{k_p}{\overset{k_d}{\rightleftharpoons}} \sum m_{n-1}+m_1 \tag{4}$$

For low concentrations of the monomer m_1 (where the polymerization as well as the depolymerization processes can be considered to be first order), the value of the equilibrium constant for the depolymerization, k_d, is given by the equation

$$K_d \sim [m_1] \tag{5}$$

The effect of temperature will then be given by

$$\log_e k_d = \frac{-\Delta H_d}{RT} + \text{constant}$$

$$\text{or } \log_e [m_1] = \frac{-\Delta H_d}{RT} + \text{constant} \tag{6}$$

where ΔH_d = heat of depolymerization

Using the values of C in Table 1 for $[m_1]$ the results shown in Fig. 6 were obtained. The depolymerization was found to be endothermic (ΔH_d equals 19·1 Kcal mole^{-1}). This value is in accord with the enthalpy changes estimated by Meadowcroft [3] for sodium phosphate glasses.

It can be seen from Fig. 6 that, on cooling, polymerization reduces the monomer concentration from 1 molar at about 900°K to 10^{-2} molar at 650°K. Thus if the rate of polymerization is fast enough to allow the glasses to equilibrate as they are quenched, the quenching operation could well eliminate the monomer. The maximum rate of quenching quoted by Meadowcroft [3] was 400° per second.

Assuming that the prior chemical reaction in the metaphosphate melt is depolymerization, equation 3 can be used in conjunction with the curves in Fig. 4 to calculate the appropriate rate constant. Thus from the slope:

$$\frac{\pi^{\frac{1}{2}}}{2} \cdot \frac{1}{K_d\,(k_d+k_p)^{\frac{1}{2}}} = 0{\cdot}8 \tag{7}$$

Comparing this slope with those of the theoretical curves derived by Delahay and Berzins [4] for first order reactions, $k_d+k_p=110$ sec^{-1}. This leads to values of $K_d=0{\cdot}1$, $k_d=10$ sec^{-1} and $k_p=100$ sec^{-1}. The final monomer concentration depends on the depolymerization rate, i.e. on k_p; from the results the half-life time is 2·303 $\log_{10}2/k_p$ or 7×10^{-3} secs. It would therefore appear that even at the fastest quenching rate, equilibrium conditions can be attained and the monomer concentrations on cooling reach negligible proportions. This fast reaction time agrees with Van Wazer's [8] estimate that molten sodium phosphates in the viscosity range of 1 poise should equilibrate in a fraction of a second.

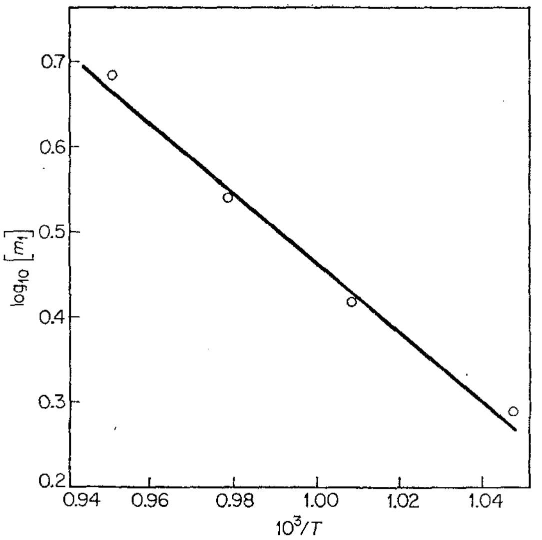

Fig. 6. Variation of monomer concentration with temperature.

Conclusions

Sodium phosphate melts are polymeric systems which are mainly mixtures of straight chain phosphates; the exact composition depends on the Na_2O/P_2O_5 ratio. The identity and the amounts present of the individual phosphates have been examined in the past by quenching followed by hydrolysis and paper chromatography for separation of the phosphates. The present electrochemical examination of sodium meta-phosphate melts has identified the presence of the three lowest polymeric species, i.e. the ortho, pyro and tripolyphosphates. There is evidence of a chemical reaction prior to electroreduction and this reaction can be associated with depolymerization. The amount of the orthophosphate monomer has been estimated; the values calculated in this way are considerably higher than those obtained following quenching. It is suggested that the quenching process allows loss of the lower polymers, particularly the monomer, through polymerization.

Since the electrochemical method can be employed in the molten phosphate system itself it appears to have some advantages over the quenching method. In addition, other glassy melts such as borates and silicates are not amenable to examination by the quenching–chromatography technique because of hydrolysis. It is proposed to examine borates and silicates by the electrochemical method.

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